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Synthesis and Solid-State NMR Characterization of ^{13}C - and ^{15}N -Labelled N-Methylphthalimide: A Model Compound for Studying Polyimides

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INTRODUCTION

High-resolution solution and solid-state NMR techniques have been used for a number of years to characterize biological and polymeric systems. However, these techniques only observe the isotropic chemical shift (δ) value and ignore the valuable information it may be obtained from the anisotropic δ tensor, which is sensitive to the structural and chemical environment. Within the last ten to twenty years, researchers have done a great deal of work determining the ^{15}N and ^{13}C δ tensor for a variety of biological systems.¹ In several of these investigations the use of dipole-coupled solid-state NMR spectroscopy has been used. This method permits the determination of both the δ tensor and its orientation with respect to the local molecular structure of the nuclei's site. From this information the solid-state structure of a system can sometimes be deduced.² Although this particular technique has been used for biological systems, its application to synthetic polymers has been rare. In addition, little has appeared regarding the magnitude and orientation of δ tensor for imides. The imide moiety is a key component in the family of polyimides which are generally semi-crystalline, heterocyclic polymers used extensively when excellent physical properties and thermal stability are required. Tensor calculations of biological polymers are usually based on model compound studies; thus, the model imide compounds [^{13}C]methylphthalimide (1), N-methyl[^{15}N]phthalimide (2), and N-[^{15}N]methylphthalimide (3) were synthesized and an analysis of NMR spectroscopic tensor elements performed in order to obtain basic information concerning the magnitude and orientation of the ^{15}N chemical shift tensors for imides, with the eventual purpose of this study to apply this information to ^{15}N -labelled polyimides.

EXPERIMENTAL

^{15}N Measurements

Solid-state CP/MAS NMR spectra were obtained on a Bruker SL-200 equipped with a Bruker MAS probe operating at 50.32 and 125.76 MHz for ^{13}C and ^{15}N , respectively. Powdered samples were packed in fused zirconia rotors fitted with Kel-F caps and spun with air, with rotation rates of 4 to 5 kHz for carbon MAS and 2 to 3 kHz for nitrogen MAS. The ^{13}C spectra were referenced to external adamantane (29.5 ppm), while ^{15}N spectra were referenced downfield from external glycine (0 ppm). The ^1H 90° pulse was 4.5 μs for ^{13}C acquisition and 6.0 μs for ^{15}N acquisition, while a mixing pulse of 2 and 50 ms acquisition were used for both nuclei. A recycle delay of 210 s, corresponding to $\sim 3-4$ ^1H T₁s, was used for observation of the nuclei. The same parameters were used to acquire static spectra except for the spinning rate, which was set to zero. ^1H T₁s were determined by monitoring the nitrogen or carbon signal using a 180°- τ -90°-CP inversion-recovery pulse sequence.

Chemical shift anisotropy (CSA) spectra were simulated using the POWFIT program developed by Dr. T. G. Oas.³ All simulations were done MicroVax 3100.

Synthesis

[^{15}N] Potassium phthalimide, [^{13}C] methyl iodide, and methyl iodide were obtained from Aldrich Chemical Company and used without purification. Dimethylformamide (DMF) was reagent grade and used as received.

A typical procedure for the preparation of an N-

methylphthalimide is as follows: A clean, dry flask was charged with equal molar amounts of [^{15}N] potassium phthalimide and methyl iodide followed by enough N,N-dimethylformamide (DMF) to give a mixture that was 15 to 20 % solids by weight. The flask was submerged in a preheated oil bath at -60°C for 2 to 3 hours. The cooled reaction mixture was poured into rapidly stirring water (10 times its volume), the precipitate collected and recrystallized from aqueous ethanol (70 to 85 % yield).

RESULTS AND DISCUSSION

The Gabriel method allows preparation of imide derivatives from methyl iodide in good yields. The ^1H T₁s were approximately 65-78 s for all protons, including the aromatic protons. ^{13}C CP/MAS NMR spectra of the model N-methylphthalimides showed multiplet peaks for the aromatic carbons which may be due to differences in crystal packing. However, the ^{15}N spectra show a single peak ($\delta_{\text{iso}} = 119.7$ ppm) for imides 2 and 3.

^{13}C and ^{15}N static powder spectra for the model imides are shown in Figures 1 and 2, respectively. For both figures the upper spectrum (a) corresponds to the singly labelled material, while the lower spectrum (b) corresponds to the doubly labelled compound. For all spectra presented the x axis is in ppm, with upfield shifts corresponding to lower ppm values. A Kaiser digital filter function⁴ was applied to the FID prior to Fourier transformation, with the α parameter set to 1 and the cutoff value varied between 3-5 ms. Even though the imides were labelled with equal amounts of isotope, approximately 500 transients were taken for the ^{15}N static spectra to achieve a signal-to-noise ratio of 100, while 32 transients for ^{13}C were taken to achieve the similar signal-to-noise. This probably reflects the differences in sensitivity between the two nuclei as well as changes in the probe's tuning characteristics in going from 50 to 20 MHz.

One of the initial purposes in synthesizing the singly ^{13}C labelled material was to obtain the unperturbed ^{13}C CSA spectrum for use in simulating the ^{15}N - ^{13}C dipolar-coupled spectrum. However, the presence of the 99% naturally abundant ^{14}N isotope clearly distorts the spectrum due to its dipolar coupling and large quadrupolar moment ($I=1$ spin). Although it is possible to simulate $I=1/2$ spins coupled to quadrupolar nuclei,⁵ such a study is beyond the scope of this work.

Figure 2 shows the ^{15}N -labelled and the ^{15}N - ^{13}C doubly labelled material. A classic anisotropic CSA spectrum was obtained for the ^{15}N -labelled compound, and from computer simulation the tensor elements δ_{11} , δ_{22} , and δ_{33} were found to be 56.4 ppm, 126.3 ppm, and 177.3 ppm, respectively. These values of the δ tensor were used for simulating the ^{15}N - ^{13}C dipolar coupled spectrum. A comparison of the experimental and simulated spectra is shown in Figure 3. The value of the dipolar coupling constant (872 Hz) indicates that the N-CH₃ bond distance is 1.52 Å. The polar coordinates α and β , which describe the orientation of the ^{15}N - ^{13}C bond vector with respect to the principal axis of the chemical shift tensor, were 88.03° and -4.39°, with the δ_{33} tensor element aligned approximately along the N-CH₃ bond (Figure 4). For our analysis, the δ_{22} tensor was assumed to be perpendicular to the imide plane; similar assumptions have been used for the amide moiety for polypeptides.¹¹

CONCLUSION

A procedure has been developed for incorporating ^{15}N and ^{13}C isotopic labelling into N-methylphthalimide, a model imide. From solid-state ^{15}N NMR spectroscopic methods the values and orientation of the δ shift tensor with respect to the N-CH₃ bond as well as the N-CH₃ bond length have been determined. Future work concerning the determination of the δ tensor for some model polyimides is in progress.

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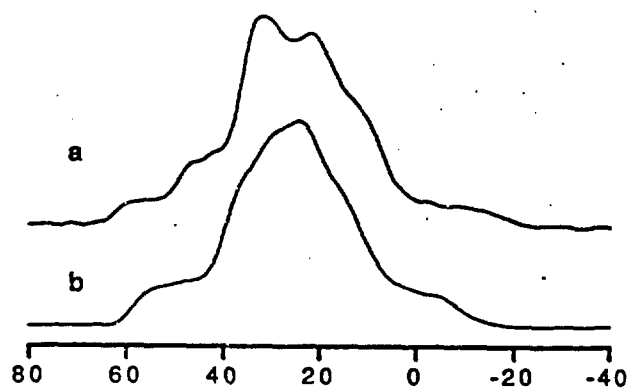


Figure 1

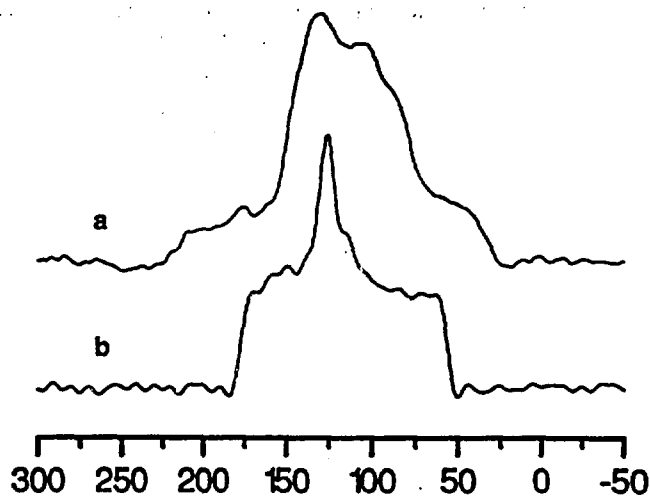


Figure 2

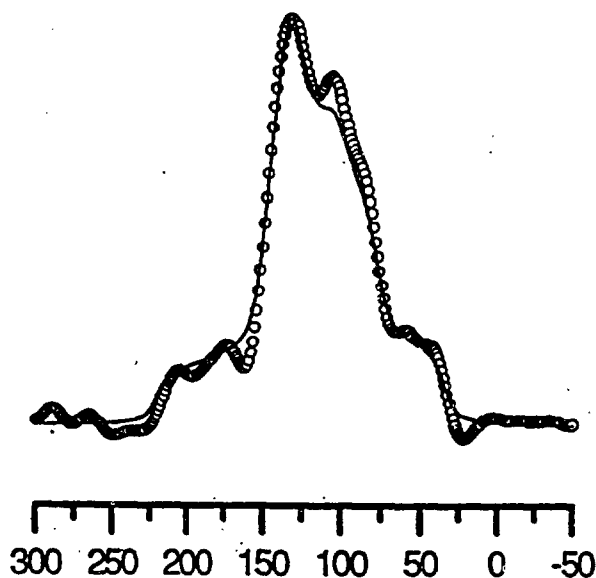


Figure 3

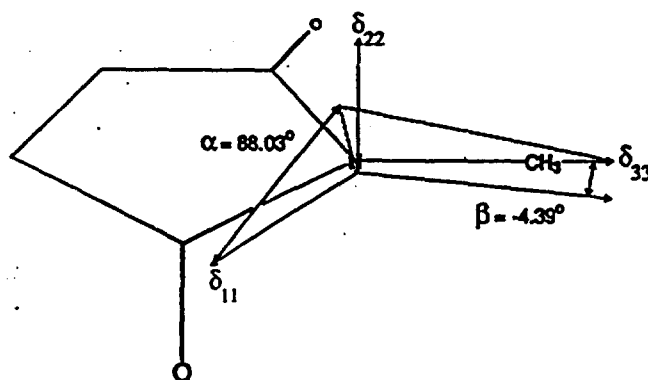


Figure 4